Progress Report: Columbia University SBRP, December, 2005

Highlight #1: Arsenic and Old Landfills

Researcher's from Columbia University's Superfund Basic Research Program are investigating arsenic mobilization and transport at two Superfund sites, the first a former municipal landfill near Augusta, ME, and the second a chemical manufacturing plant in Vineland, NJ.

Here we highlight results related to arsenic mobilization at the landfill. The levels of groundwater arsenic below and near the former landfill (about 300 µg/L) are significantly elevated above the US EPA's new Maximum Contaminant Level (MCL) for arsenic (10 µg/L). We conclude that elevated groundwater arsenic concentrations at the site are of natural origin, with arsenic being mobilized by the interaction of highly reducing landfill leachate with underlying sediments. This conclusion is supported by several lines of evidence including: (1) arsenic sediment concentrations that are similar on and off site, i.e. there are no arsenic hotspots, (2) non-uniform distribution of the sediment measurement of chemical oxygen demand, which is consistent with landfill leachate inputs being responsible for the strongly reducing conditions, and (3) laboratory batch incubation experiments that show reducing conditions are able to mobilize As from aquifer sediments.

Arsenic is listed as a contaminant of concern at over 700 US Superfund sites, making it the second most common contaminant after lead. Approximately 35% of these sites involve landfills; improper disposal of arsenical wastes is probably responsible for this contamination at some fraction of these sites. However, our results suggest that reducing conditions generally induced in groundwater by landfill leachate have the potential to mobilize natural As as well.

At our landfill site, naturally occurring arsenic concentrations in the sediment of about 5 mg/kg and redox buffer capacity of these sediments have seriously limited the effectiveness of remediation efforts. These have included installation of a clay cap, a vapor extraction system, and a groundwater extraction and treatment system, which have been effective at appreciably lowering concentrations of dissolved volatile organic compounds such as dimethyl formamide (DMF), the original culprit and reason this site was included on the National Priorities List. These efforts have not, however, been effective at reducing concentrations of dissolved arsenic. In addition, a pilot field experiment assessed the potential of *in situ* oxidation as a remediation option. Capping, one of the most common remediations done at landfills to stop precipitation from infiltrating through the landfill material, has not proved effective at this site on the time scale of ~15 years in lowering dissolved As concentrations in the aquifer, because the mobilization of naturally occurring As will continue until the large amount of readily available organic matter deposited by landfill leachate is exhausted. Potentially more promising directions for remediation are suggested by additional laboratory experiments on Winthrop sediments which demonstrated that enhancing native microbial communities by adding a carbon source could decrease dissolved arsenic levels and

that the liability of arsenic in mineral phases was decreased by this process. These findings indicate that enhanced sulfate reduction merits further study as a potential *in situ* groundwater arsenic remediation strategy at landfills and other similar sites.

Along with staff from Region 3 of the NYS Department of Environmental Conservation, we built on these results by investigating the potential of old unlined landfills to mobilize arsenic, sharing field and laboratory efforts on samples collected at several old landfills.

We are currently investigating the potential of whether arsenic/iron ratios in iron flocculates, which commonly appear at surface seeps or springs near landfills, can be used to predict arsenic mobilization issues at a landfill. Bright orange in color and composed predominantly of amorphous iron oxyhydroxides, iron flocs provide advantages as a triage tool in that they are very easy to locate, collect and measure. To date only a limited number of old landfills in Region 3 have been investigated, and six of the seven of these had elevated As/Fe ratios in the iron flocs, underlining the importance of the mechanisms identified in our initial work on the landfill site in Maine.

For More Information Contact:

Steven N. Chillrud, PhD
Lamont-Doherty Earth Observatory of Columbia University
Tel: 845-365-8893
Fax: 845-365-8155
Email: chilli@ldeo.columbia.edu

H. James Simpson, PhD
Lamont-Doherty Earth Observatory of Columbia University
Tel: 845-365-8570
Fax: 845-365-8155
Email: simpsonj@ldeo.columbia.edu

To learn more about this research, please refer to:

Keimowitz, A. R., H. J. Simpson, M. Stute, S. Datta, S. N. Chillrud, J. Ross and M. Tsang. 2005. Naturally-occuring arsenic: mobilization at a landfill in Maine and implications for remediation. Applied Geochemistry 20: 1985-2002.

Keimowitz, A. R., H. J. Simpson, S. N. Chillrud, M. Stute, M. Tsang, S. Datta and J. Ross. 2005. Oxidation of groundwater arsenic and iron. In: Advances in Arsenic Research: Integration of Experimental and Observational Studies and Implications for Mitigation. ACS Symposium Series, vol. 915. P. A. O'Day, D. Vlassopoulos, D. Meng and L. G. Benning, Eds. American Chemical Society: Washington, DC.

Keimowitz, A. R., Y. Zheng, S. N. Chillrud, B. J. Mailloux, H. B. Jung, M. Stute and H. J. Simpson. 2005. Arsenic redistribution between sediments and water near a highly contaminated source. Environmental Science & Technology. 39: 8606 – 8613.

Highlight #2: Modification of Risk of Arsenic-induced Skin Lesions by Sunlight Exposure and Tobacco Smoking in Bangladesh

Inorganic arsenic (As) is often present in soil and drinking water due to both natural and man-made sources. The presence of As in groundwater has been related to elevated risks of premalignant and malignant skin lesions and internal cancers. Cutaneous abnormalities including melanosis and keratosis have long been known as early signs of chronic inorganic As poisoning. The literature has documented marked inter-individual variability in susceptibility to adverse effects of As exposure from drinking water. We performed a cross-sectional analysis to evaluate the influences of tobacco smoking and excessive sunlight exposure on the relation between As exposure from drinking water and risk of skin lesions using baseline data of 11,062 cohort members from the Health Effects of Arsenic Longitudinal Study (HEALS) in Araihazar, Bangladesh (Project #3). A time-weighted well As concentration (TWA) was estimated for each participant by incorporating the information on well use history. Relative excess risk for interaction (RERI) and its 95% confidence intervals (CI) were estimated to assess the synergy of TWA with sunlight exposure and tobacco smoking using adjusted prevalence odds ratios (PORs). Because distributions of tobacco use are very different by gender, gender-specific analysis was performed. As women in Bangladesh universally wear traditional dresses that almost completely cover the skin of their trunk, sunlight exposure of female respondents was considered minimal and therefore was not assessed in the study.

In men, compared to never-smokers with lowest level of TWA (< 28.1 µg/L), the PORs for skin lesions associated with medium and high levels of TWA (28.1-113.0 and 113.1-864.0 µg/L) were 2.4 (95% CI: 1.3-4.4) and 2.4 (95% CI: 1.3-4.5) among never-smokers, while the PORs in increasing levels of TWA were 1.0 (95% CI: 0.6-1.9), 2.6 (95% CI: 1.5-4.4), and 4.0 (95% CI: 2.4-6.9) among ever-smokers. We observed a significant synergistic effect between highest level of TWA (113.1-864.0 µg/L) and tobacco smoking on risk of skin lesions in men (RERI: 1.5, 95% CI: 0.3, 2.7), indicating that the *excessive* risk due to joint exposure to tobacco smoking and highest level of TWA is 1.5 times the background risk (the risk in never-smokers with the lowest level of TWA). When ever-smokers were further grouped into past, current moderate, and current heavy smokers, the synergistic effects of highest level of TWA with past and current heavy smoking were stronger, with RERIs being 2.8 (95% CI: 0.1, 5.6) and 2.0 (95% CI: 0.1, 4.0), respectively. Patterns of PORs in women indicate similar but much weaker interaction effects of TWA with tobacco smoking. Other epidemiologic studies have also reported elevated risks of bladder and lung caner associated with high level of As exposure among cigarette smokers compared to non-smokers.

Compared to men without excessive sunlight exposure and with lowest level of TWA, the PORs for skin lesions associated with medium and high levels of TWA were 2.5 (95% CI: 1.9-3.5) and 3.8 (95% CI: 2.8-5.1) among men without excessive sunlight exposure, while the PORs in increasing levels of TWA were 2.0 (95% CI: 1.0-3.9), 4.5 (95% CI: 2.6-7.8), and 5.3 (95% CI: 3.0-9.3) among men with excessive sunlight exposure. This observation is in line with the mounting evidence from animal studies that As may cause skin tumors by enhancing the mutagenicity of ultraviolet radiation (UVR) possibly through inhibiting DNA repair and/or enhancing positive growth signaling.

The high prevalence of tobacco smoking in Bangladesh has been noted as a major public health problem. In our study population, 74% and 62% of men were ever and current smokers of tobacco products. An emphasis on smoking cessation programs in Bangladesh and around the world would be prudent, particularly in areas with high levels of As exposure. Our findings also suggest that various lifestyle and occupational factors, rather than simply a detection bias, contribute to the much higher risk of As-related skin lesions in men that has been observed in other studies. Epidemiologic studies that investigate interaction effects are often criticized for dichotomizing exposure levels. Importantly, we assessed dose-specific interaction on the additive scale and showed that the synergy between lifestyle factors and As exposure is sometimes dose-dependent. The identification of factors that render an individual more likely than others to be affected by As exposure may help unravel disease mechanisms and design appropriate remediation measures. Since most As-induced skin cancers arise from these skin lesions, treatment and remediation plans should take into consideration these etiologic co-factors.

For More Information Contact:

Habibul Ahsan, MBBS, MMSc
Associate Professor of Epidemiology
Mailman School of Public Health
at Columbia University
722 West 168th Street
New York, NY 10032

Tel: 212-305-7636
e-mail: ha37@columbia.edu

To Learn More About This Topic, Look for the Upcoming Paper:

Chen, Y, Parvez, F, Graziano, JH, Hussain, AZM I, Momotaj, H, Howe, GR, Ahsan, H: Modification of risk of arsenic-induced premalignant skin lesions by sunlight exposure, smoking, and occupational exposures in Bangladesh. In Review, 2005.

Project 1: Bioavailability of Soil Lead and Arsenic in Humans
P.I.: Conrad Blum

The primary aims of this project are to 1) determine estimates of the bioavailability of lead in soils from a mining site, smelting site and urban site; 2) to test the hypothesis that phosphate-based soil amending agents reduce this bioavailability in adult humans; and 3) to examine the correlation between the human and *in vitro* estimates of bioavailability in these soils. This study involves the ingestion of tiny amounts of sterilized soils, which contain lead but no other contaminants of concern. The method utilizes the technique known as stable isotope dilution, and takes advantage of the fact that the presence of non-radioactive isotopes of lead in soil allow one to track tiny amounts of lead that are actually absorbed into blood.

A total of 20 volunteer subjects have completed the protocol designed to assess the bioavailability of lead in soil. The first twelve study participants were randomly assigned to ingest either the phosphate amended or non-amended soil. This soil from a former smelting site in Joplin, MO, was treated with 1% phosphate at the site, by the U.S. EPA, and sampled at 6 month intervals. We have evaluated an "amended" and "non-amended" soil specimen that was sampled 18 months post-treatment. Final Pb isotope and bioavailability data were analyzed in the Geochemistry Core Laboratory.

The findings, discussed in last year's report, are extremely interesting and potentially important. Among the six subjects who received the non-amended soil, the mean Pb bioavailability was 34.7%. In contrast, among those who received the phosphate-amended soil, mean Pb bioavailability was 19.9%, significantly less. While there is a wide range of inter-individual variability, this represents an average reduction in bioavailability of 43%. Studies evaluating the bioavailability of these same soil samples in animals, by Casteel et al, and in an *in vitro* system, by Ruby et al, reported a 38% reduction in bioavailability, by both methods, validating the relative effect that phosphate inactivation has on soil lead bioavailability in these samples. It is particularly important to note that our work to date appears to validate the use of the *in vitro* and animal models, in that the values obtained for bioavailability in all three systems are coherent with each other.

This project will be coming to a close, and we have not chosen to request additional funding for this work in our recent competitive grant renewal application.

Project 2: Genotoxic Mechanisms of Arsenic in Mammalian Cells
P.I.: Tom K. Hei

The overall goals of this project focus on 1) the mechanisms of the DNA damaging effects of arsenic in mammalian cells, particularly the role of mitochondrial DNA mutations and the subsequent induction of reactive oxygen and reactive nitrogen species; and 2) the mechanism for arsenic-induced apoptosis (programmed cell death) in melanoma cells. During the current funding period, we found that treatment of human-hamster hybrid (A_L)

cells with a 1.75 μg/ml dose of sodium arsenite for five days (survival level of ~ 22%) resulted in a consistent loss of mtDNA. The findings were based on southern blotting using random-primed ^{32}P-labelled mtDNA as probe. The observation is consistent with our recent observation that mitochondrial DNA deficient (rho zero) cells are significantly less responsive to the mutagenic effects of arsenic.

Dr. Graziano's group (Project 4) recently reported evidence that exposure of children to arsenic in drinking water is associated with reduced intellectual function. This is consistent with our recent observation that the non-differentiated rat PC-12 cells, which are neuronal in nature, are extremely sensitive to sodium arsenite treatment, responding by the development of apoptosis and secondary necrosis 6 hours after treatment. Using poly-D-Lysine as coating matrix and neural growth factor beta (NGFβ 100 ng/ml for 4 days), we have succeeded in establishing differentiated PC-12 cell culture. Furthermore, similar to the non-differentiated cells, these differentiated PC-12 cells (in the absence of NGFβ) showed a seven-fold increase in apoptosis following treatment with sodium arsenite (5 μM for 16 hr). Concurrent treatment of these arsenite-exposed cells with either LY294002 (a specific inhibitor of phosphatidylinositol 3-kinase) or NS398 (a specific inhibitor of cyclooxygenase-2) further enhanced the apoptotic incidence. Since the PC-12 cells, in the presence of NGFβ exhibit many of the phenotypic characteristics of differentiated neurons, our findings provide evidence that the PC-12 model is an excellent model in evaluating the induction and mechanism of arsenite toxicity to neuronal cells.

Arsenic is an important environmental carcinogen that affects millions of people worldwide through contaminated water supplies. For decades, arsenic was considered a non-genotoxic carcinogen. Using the highly sensitive A_L mutation assay, we showed previously that arsenic is indeed a potent gene and chromosomal mutagen and mitochondria are a primary target in arsenic-induced genotoxic response. A better understanding of the mutagenic/carcinogenic mechanism of arsenic should provide a basis for better interventional approach in both treatment and prevention of arsenic induced cancer. On the other hand, melanoma is often a deadly disease due to the lack of effective treatment options. Despite the dramatic increase in the incidence of malignant melanoma in the past decades, the molecular mechanisms of its progression and extreme resistance to treatment, which kill cells by induction of programmed cell death (apoptosis), remain largely unknown. Our present study, however, indicates that arsenic can also be a two sided sword and could, potentially, benefit thousands of melanoma patients each year who fail conventional therapeutic regimens.

Project 3: A Cohort Study of Health Effects of Arsenic Exposure in Bangladesh
P.I.: Habibul Ahsan

This prospective cohort study recruited 11,746 men and women (with 98% response rate) in Araihazar, Bangladesh, during 2000-2002 to investigate the health effects of arsenic exposure, with an initial focus on skin lesions and skin cancers, and also to establish a biorepository for future studies. In order to build a sampling frame, we tested all 5,966 contiguous tube wells for arsenic within a well-defined area of approximately 26 square kilometers in collaboration with our hydrology and geochemistry colleagues and enumerated all 65,876 people in the study area using these wells. Findings from this pre-cohort study survey are published in a series of papers [van Geen et al., 2002 and 2003; Parvez et al., 2005]. The biological samples have been processed and baseline questionnaire data have been processed and stored for all 11,746 cohort members. The design of this multidisciplinary project with a description of the cohort was published [Ahsan et al., 2005]. We already completed the analysis of total urinary arsenic of all these individuals at baseline and also arsenic metabolites in a subset of 1,200 individuals (skin lesion cases and controls). Using baseline cross-sectional data on arsenic exposure and prevalent skin lesion cases we have conducted full dose-response analyses of the relationship between arsenic exposure and risk of skin lesions and factors modifying this dose-response effect. These novel results, with major public health significance, are being published [Ahsan et al., submitted; Argos et al., 2005; Chen et al., submitted]. We have also collected full dietary data from all 11,746 cohort members using a modified meal-based dietary questionnaire and have validated this instrument [Chen et al., 2004].

Between October 2002 and May 2004, we completed our first 2-yearly follow-up visits of the entire cohort. We were able to collect follow-up data on nearly 100% (11,686 of the total 11,746) of the baseline cohort. A total of 11,328 individuals completed the follow-up interview and clinical evaluations; 254 had migrated, 104 died and 60 could not be found. A total of 11,109 individuals (of 11,328 completed interview and clinical evaluations) provided urine samples. The follow-up data on all 11,746 individuals have been computerized. All 11,109 follow-up urine samples have also been analyzed for urinary total arsenic. In addition, we also analyzed blood arsenic levels for the newly identified skin lesion cases from this follow-up visit and their matched controls. Findings from this prospective investigation of the association between blood arsenic and skin lesion risk are being published [Chen et al., submitted].

Our second 2-yearly follow-up visits started in October, 2004; to date, we completed in-person follow-up home visits and have collected questionnaire, clinical data and biological samples from 9,500 of our cohort members with similar response rates for different types of data as our first 2-yearly follow-up.

In addition to the above-mentioned components, the findings and resources from this prospective cohort study have also yielded many other ancillary studies and

publications including three additional R01 grants from NIH to investigate the genetic and nutritional aspects as well as chemoprevention of arsenic health effects.

Project 4: Environmental Arsenic, Pregnancy and Children's Health
P.I.: J. Graziano

Chronic exposure to arsenic (As) and manganese (Mn) has been taking place in Bangladesh for more than three decades due to the consumption of groundwater that is naturally elevated in both elements. We recently reported findings from a cross-sectional study of 10 year-old children in Bangladesh that found an adverse association between As exposure and cognitive function in children. Since Mn is also known to be neurotoxic, we subsequently conducted an additional study of 10 year-olds to test the hypothesis that water-borne Mn exposure might also be neurotoxic in children.

Our original study of As in 201 ten year-olds included 54 children using wells with low As concentrations, i.e., ≤ 10 µg/L. In our subsequent field work, we recruited 88 additional children drinking from wells comparably low in As. Here we report on associations between water Mn and intellectual function in children in the combined sample of 142 children.

The mean water Mn concentration was 795 µg/L, with a range of 4 to 3908 µg/L; by comparison, the World Health Organization (WHO) maximal contaminant level is 500 µg/L. By design, the range of water As concentrations was narrow (0.1 to 10 µg/L), with a mean of 3.0 µg/L.

Linear regression analyses, which predict raw test scores from the socio-demographic features retained in the final "core" model, as expected, revealed better scores among children who: 1) had more educated mothers; 2) lived in more adequate dwellings; 3) had access to television; 4) were taller; and 5) had a larger head circumference (data not shown). Collectively, these factors explained 25.0%, 24.1%, and 17.7% of the variances in Full Scale, Performance, and Verbal raw scores, respectively.

Prior to adjustment for sociodemographic factors, water Mn was significantly associated with Full Scale, Performance, and Verbal raw scores, explaining 10%, 10%, and 4%, respectively, of the variances in scores. After adjusting for sociodemographic factors, water Mn concentration remained significantly and negatively associated with all three scores, explaining incremental portions of the variances in Full, Performance and Verbal scores.

The addition of water As to these regression models failed to change the pattern of associations between intellectual function and sociodemographic variables, or between intellectual function and water Mn. Given the extremely low levels of water As, water As was not significantly associated with intellectual function. Similarly,

associations between water Mn and intellectual function scores were unchanged when we adjusted for both urinary As and urinary creatinine.

In order to examine the dose-response relationship between water Mn and intellectual function, we subsequently stratified children into four approximately equal-sized groups, based on well water Mn. After adjustment for other factors that influence child intelligence, children in Groups 1 and 4 were significantly different for Full Scale, Performance, and Verbal scores. Compared to Group 1, children in Groups 2 and 3 had lower, albeit not significantly so, Full Scale and Performance. Verbal score comparisons between children in Groups 2 and 3 and those in Group 1 were in the expected direction but did not approach significance.

Project 5: Arsenic mobilization in Bangladesh Groundwater

Co-P.I.'s: Y. Zheng and M. Stute

Progress reported last year resulted in three manuscripts, Zheng et al. (GCA, in press) finds deeper aquifer as a sustainable drinking water source for Bangladesh; Stute et al (WRR, submitted) attributes the spatial patterns of As in shallow aquifer to flushing; Dhar et al. (GCA, in prep) will report on temporal trends and variability of groundwater As and other dissolved ions based on 3-yrs of data of 37 monitoring wells in Araihazar. Three additional manuscripts (one in revision, 2 in prep) are based on advances made in 2005:

Calibrating a Sequential Extraction Method for Speciation Analysis of As in Natural Samples

PhD candidate Hun Bok Jung (Jung and Zheng, Water Research, in revision) conducted a series of laboratory experiments to establish a method that will allow quantitative determination of As oxidation state in natural sediment samples. This is important because synchrotron X-ray Spectroscopy is not sensitive enough to assay whether As present at natural abundance in sediment is As(III) or As(V). By adding 0.1 M L-ascorbic acid to 1 M phosphate solution, 80~100% of As(III) sorbed onto various Fe and Mn oxides was recovered under anaerobic conditions.

Mineralogy and Mobility of Fe and As in Meghna River Sediments in Bangladesh

Post-doc Saugata Datta (now assistant professor at W. Georgia State Univ.) undertook a geochemical study of sediment samples taken along the Meghna River in January 2003. The most surprising finding was that sub-surface sediment samples (depth 1 to 4 m below surface) contained 0.2 to 1300 mg/kg phosphate-extractable As and 0.8 to 23700 mg/kg HCl-extractable As. In contrast, surficial sediments from the same locations contained 10-20 mg/kg total As. Much of the subsurface sediment As (10-100%) is phosphate extractable, is not likely associated with acid soluble sulfide, and is most likely sorbed to Fe-minerals such as magnetite or goethite determined by

EXAFS. Mixed valence states of As are found by XANES and voltammetric speciation of P-ext As analyses. The source and fate of this As require further study.

Stable Isotope (^{18}O, ^{2}H) and Arsenic Distribution in the Shallow Aquifers in Araihazar, Bangladesh

We have monitored for about a year the oxygen (^{18}O) and hydrogen (^{2}H) isotopic composition of precipitation in Dhaka, Bangladesh, and of surface waters and groundwaters in a 25 km^2 study area in Araihazar upazila ($90^{o}37'E$, $23^{o}74'N$), about 30 km east of Dhaka. The groundwater isotopic composition obtained at 6 multi level well sites covers the range between the global meteoric water line and moderately evaporated surface waters. These data indicate that some groundwaters are recharged directly by precipitation while others show evidence of recharge from evaporated surface waters during the wet and at the beginning of the dry season. Using the deuterium excess as an estimator of the degree of evaporation, the wells show characteristic changes from more or less evaporated sources of water as a function of depth. The degree of evaporation expressed as deuterium excess does not correlate with As concentrations in the groundwater samples. This finding suggests that the source of groundwater recharge from either precipitation with a low reducing capacity, or surface waters with a higher reducing capacity, is not an important factor in As mobilization.

Project 6: Redistribution of Arsenic and other contaminants at sites in New Jersey and Maine
Co-P.I.'s: H.J. Simpson and M. Stute

Project six focuses on investigation of arsenic mobilization and transport at two Superfund sites, the first an old municipal landfill in Winthrop, ME and the second a chemical manufacturing plant in Vineland, NJ. This year our senior graduate student, Alison Keimowitz, was lead author on 3 peer reviewed journal publications, completed her PhD dissertation which was focused on arsenic transport and fate issues at our study sites, and was awarded a Fulbright Fellowship. In the first manuscript published in the Applied Geochemistry, we conclude that elevated groundwater Arsenic concentrations at the Winthrop Superfund site are of natural origin, with arsenic being mobilized by the interaction of highly reducing landfill leachate with underlying sediment. Approximately 35% of US Superfund sites where arsenic is a contaminant of concern involve landfills (EPA, 2005); improper disposal of arsenical wastes is probably responsible for this contamination at some fraction of these sites. However, reducing conditions generally induced in groundwater by landfill leachate have the potential to mobilize As at these sites as well as many old landfills. We have followed up investigations concerning the potential of old unlined landfills to be mobilizing arsenic with staff from Region 3 of the NYS Department of Environmental Conservation, including shared field and laboratory efforts on samples collected at several old landfills

and one submitted collaborative manuscript. This collaboration has focused on developing As/Fe ratios in iron flocs which commonly appear at surface seeps near landfills as a predictive tool of arsenic mobilization issues being present at a landfill. Roughly ¾ of the old landfills investigated to date in Region 3 have had elevated As/Fe ratios.

Additional fieldwork during the last year has focused on collection of samples from the Vineland site for tracer measurements and for characterization of the potential for As mobilization in aquifer solids. We collected 24 samples for SF_6 and $^3H/^3He$ on extraction and monitoring wells, which will allow us to determine groundwater ages for the aquifer underneath the site. The SF_6 analyses show a characteristic decrease of age as a function of depth. The tracer data set will allow us to compare how the operating pump & treat system has influenced the groundwater flow regime by comparison with an earlier survey and eventually will be used as calibration target of the existing groundwater flow model that then is needed to determine locations of additional wells to ensure capture of the arsenic plume. Preliminary characterization of the aquifer solids suggests that the vast majority of the arsenic is easily mobilizable. This is a promising preliminary result relevant to proposed field experiments focused on assessing feasibility of in situ mobilization of arsenic as a way to greatly enhance the pump and treat remediation of the site.

Project 7: Assessment and Remediation of As in groundwater
P.I.: Alexander van Geen

This year saw the publication of two papers describing significant advances in the application of iron filings as a medium for removing arsenic. The first, by Nikolaidis et al. which appeared in a volume of the ACS Symposium Series devoted to As, demonstrates that the medium can be used at the household level in Bangladesh to treat groundwater containing elevated As concentrations. The second, by Cheng et al. which appeared in Env. Sci. & Technol., showed that some (but not all) organic As species abundantly present in groundwater at the Vineland Chemical Superfund site in New Jersey can effectively be removed by passage through a column of Fe filings. The significance of this work is that the polishing of plant effluent with Fe filings could significantly reduce the cost of pump and treat operations at the site, as state standards for the composition of the effluent from the plant become more stringent.

This year also saw the publication of three studies addressing the fundamental controls of As mobilization in reducing aquifers. The first, by Cheng et al. which appeared in Env. Sci. Technol., demonstrated that temporal variations in groundwater As concentrations can be significant but are limited only to the very shallowest (i.e., <10 m deep) aquifers of Bangladesh. This is consistent with groundwater dating conducted under Project 5 showing that seasonal and interannual variations in groundwater composition are likely to be dampened in older, deeper strata. The second paper, by Thoral et al. which also appeared in Env. Sci. Technol., shows that the presence of As

significantly alters the process of Fe(II) oxidation and limits the size of Fe oxide particles to the point where As removal by filtration is hampered. Beyond practical implications for treatment, the formation of relatively mobile As-enriched Fe colloids in response to seasonal redox fluctuations could play a significant role in propagating changes in surface forcing to naturally enriched, shallow aquifers. The third paper, by van Geen et al., scheduled to appear in Chemical Geology, has provided complementary information on the processes prevailing in shallow aquifer by mapping the distribution of groundwater and sediment properties at an unprecedented spatial resolution of ~100 m laterally and ~2 m vertically. The new observations, when linked to hydrological and geophysical observations in the same study area of Bangladesh, show that despite tremendous variability, groundwater As concentrations in shallow aquifers are predictably related to local variations in recharge and groundwater flow.

Project 7 also continues to direct efforts to lower As exposure in Columbia University's study area in Bangladesh, while extracting generalizable lessons from these activities. A significant finding, published by van Geen et al. in Env. Sci. Technol., has been that the field-kit for As that is presently most widely used in Bangladesh performs rather well in terms of As detection in groundwater. In a forthcoming paper in Health & Place that the mere testing and labeling of tube wells, coupled with the installation of 50 deep, arsenic-free community wells has induced two-thirds of the exposed population to change their source of water.

Administrative Core

Director: Joseph Graziano
Deputy Director: Alexander van Geen

A. General Activities: The Administrative Core, which includes the information dissemination program that is discussed below, continues to function smoothly, and was instrumental in directing the creation and submission of a successful competitive renewal application of our SBRP program. Dr. Graziano, the Program Director, and Dr. van Geen, the Associate Director, communicate virtually every working day with regard to the integration of our biomedical and non-biomedical research programs. This communication is evidenced by the number of truly multi-disciplinary publications that have come from our program, involving close collaboration between biomedical, earth, and social scientists. Our monthly two-hour seminars (one hour biomedical and one hour non-biomedical) are exceptionally well attended. We believe that our SBRP is unique with regard to the extent that these two dimensions of the program are highly integrated.

In March, 2005, our External Advisory Committee convened for two days at Columbia University's Lamont-Doherty Earth Observatory to review past progress as well as the new proposed specific aims for our competitive renewal application. The composition of the committee has been revised somewhat to reflect the new program

aims, and now includes only three members of the former committee: a) Chien-Jen Chen, Committee Chair, and Chairman of the Graduate Institute of Taiwan; b) Andrew Gelman, Professor of Statistics at Columbia University; and c) Alan Welch, Geochemist, U.S. Geological Survey (USGS). New members include: d) Zoltan Szabo, Research Hydrologist, USGS; e) Margaret Karagas, Chair, Section of Biostatistics and Epidemiology, Dartmouth University; f) Allan Smith, Professor of Epidemiology, University of California, Berkeley; g) X. Chris Le, Professor of Public Health Sciences, University of Alberta; h) Peggy O'Day, Associate Professor of Natural Sciences, University of California, Merced; and i) James Davis, USGS. Several of these senior scientists were selected because they are also potential future collaborators. This newly assembled committee was extremely instrumental in guiding the future direction of many of the projects and core laboratories. The committee will reconvene in the Spring of 2006.

B. Information Dissemination and Transfer, Government Liaison, and Outreach Activities
P.I.: Meredith Golden

Information Dissemination and Transfer, Government Liaison, and Outreach Activities, operating out of the Administrative Core, have been played an integral role in the Columbia SBRP research and training programs. The overriding objective has been to make available the scientific findings and products generated from Columbia's interdisciplinary suite of projects related to the bioavailability of soil lead in humans and the bioavailability, health effects, and geochemistry of arsenic. The communication of new knowledge among scientists, policymakers, and the private and public sectors is essential to stimulate pioneering research, highlight the most urgent priorities, generate innovative products, and ensure effective policies.

The Columbia SBRP distributes online information regarding its projects and seminars through the program website and its electronic distribution lists to a diverse audience of students, educators, researchers, policymakers, private entrepreneurs, non-profit advocates, and the general public. The extensive network of nearly 1500 individuals facilitates frequent correspondence among those in the US and around the world interested in environmental pathways and human health effects from lead and arsenic. The Columbia SBRP Monthly Seminars serve as a dynamic forum for both the program scientists and others concerned with these issues. Each seminar includes two or more presentations highlighting biomedical and geoscience topics. The informal discussions that follow the presentations help enhance the quality of these studies and encourage the applications of the program's findings.

Information dissemination and outreach play an ongoing role in the individual research projects and lab cores. Columbia scientists work with policymakers, private stakeholders, commercial firms, and non-profit groups to better understand the information needs of these parties and potential applications for the SBRP research findings. Inside the classroom, several SBRP scientists have incorporated their research into undergraduate and graduate courses. Consequently, more students

attend the SBRP seminars, become involved in SBRP projects, and incorporate related research into their theses and publications. This year five students and post-doctoral fellows from the Mailman School of Public Health and Lamont-Doherty Earth Observatory have presented their research projects and findings at the SBRP seminars. The seminars provide them with a unique opportunity for feedback from an interdisciplinary audience. The Columbia SBRP also encourages and enables students to participate in national and international scientific meetings.

In response to the SBRP's urgent request for geospatial expertise following Hurricane Katrina, Columbia worked with other SBRP programs to provide key maps and data for the new NIEHS website created to assist public health and emergency workers in the affected areas. The Columbia SBRP also participated in the NIEHS meeting on Integrated Earth Observations: Applications to Air Quality and Human Health and the SBRP Bioavailability Workshop. Finally, Columbia, as a member of the SBRP Outreach/Research Translation Planning Committee, has been actively involved in preparations for the next SBRP annual meeting that will take place on 12-13 January 2006 in New York City. Columbia's information dissemination and transfer, government liaison, and outreach activities help ensure that the university's SBRP research continues to be relevant and accessible to a broad range of academic, government, and community groups.

Core A: Trace Metals Core
P.I. Joseph Graziano
Laboratory Director: Vesna Slavkovich

The Trace Metals Research Support Core currently provides analytical support to three of the biomedical research projects under this SBRP, i.e., Projects 1, 3 and 4. The Core has the capability of measuring a broad range of metals and metalloids in biological samples, including Pb, Hg, As, Cd, Mn, Fe, Cu, Zn, Cr, Co, Pt, K and others. In addition, a number of simple biochemical assays are performed so as to allow for the interpretation of the metal concentration data. During the past year, the laboratory carried out various analyses of nearly 20,000 biological samples.

To date, during the six year course of this SBRP, this laboratory has received, processed, analyzed and stored more than 80,000 biological samples from various epidemiologic studies, all of which remain archived for future additional exploration. Two Perkin-Elmer AAnalyst 600 Graphite Furnace Atomic Absorption Spectro-phometers have been the workhorses of the lab. In addition, a Perkin-Elmer Elan II DRC Mass Spectrometer, installed last year, has contributed heavily to many major new findings. During the past year, we have continued to use these instruments to conduct analyses of total arsenic and arsenic metabolites in urine from participants in projects 3 and 4, as well as in Dr. Mary Gamble's RO1 grant concerning nutritional influences on arsenic metabolism. Collectively, these analyses have revealed that: a) individuals who have a relatively high proportion of monomethyl arsenic acid (MMA) in urine are at increased risk for skin lesions; b) the methylation of arsenic is saturable; c) serum folate concentrations are negatively correlated with the proportion of MMA in urine; d) folate

supplementation to folate deficient individuals reduces the proportions of inorganic arsenic and MMA in urine and increases the amount of dimethylarsenic (DMA) in urine; e) blood arsenic concentrations, measured by ICP-MS, are a useful biomarker of arsenic exposure and are associated with the risk of skin lesions; and f) there is a strong correlation between maternal and cord blood arsenic concentrations. In addition, the laboratory supported research from project #4 which has revealed that water manganese exposure is associated with cognitive deficits in ten year-old children.

An exciting new development has been the establishment of a method to measure extraordinarily low concentrations of arsenic metabolites in blood. Using mother-cord blood pairs (and maternal urine samples) derived from project #4, we have determined that a) the profile of concentrations of arsenic metabolites (arsenite, arsenate, MMA and DMA) in the blood of newborns is virtually identical to that of their mothers; and b) the profiles of arsenic metabolites in blood is *extremely* different than that in urine, in that blood contains far more of the toxic metabolites (i.e., arsenite and MMA) than urine.

In summary, this laboratory has been successfully supporting numerous landmark studies of arsenic and manganese. In its most recent review by study section, the laboratory received a priority score of 1.2.

Core B: Geochemistry Core
Steven N. Chillrud and Alexander van Geen, co-Directors
Zhongqi Cheng and James Ross, lab managers

This analytical core laboratory is housed at Lamont-Doherty Earth Observatory (LDEO). It provides sample preparation and analyses to six projects of the Columbia Superfund program (biomedical projects 1, 3 and 4 and earth science projects 5, 6 and 7) and trains students and post-docs. Sample preparation and analyses are carried out for water, soil, sediment, leachate, plant material and pre-ashed blood samples. As such the majority of the publications and exciting new discoveries from these projects have been directly linked to the contributions from this core. For example, the analyses of manganese concentrations, in addition to arsenic, for >3,000 Bangladesh groundwater samples enabled the statistical analyses of manganese exposure and health effects by the health science group – which led to the first ever link between water manganese and child intelligence (Project 4).

Analyses on environmental and geological samples from Bangladesh, Vineland, NJ, Winthrop, ME and several NYS landfills together with training of students in analytical techniques have been the major focus in the past year. Joy Ann Mahabir (summer intern), Karrie Radloff (GRA in Earth and Environmental Engineering), Amy Schoenfeld (GRA in Earth Science Journalism), Zahid Aziz (GRA in Earth and Environmental Sciences), Karen Wovkulich (GRA in Earth and Environmental Sciences), Ratan Dhar (Queens College GRA working on project 5), Hun Bok Jung (Queens

College GRA worked on project 5), Yi He (Queens College GRA worked on project 5), Jérôme Métral, and Fanny Travassac (two French students working on our collaborative research in Bangladesh) have all received training in a wide variety of analytical techniques, and each completed large number of analyses under the guidance of Dr. Cheng and Mr. Ross.

This year also saw the publication of an analytical method paper in Applied Geochemistry on determining lead isotope ratios in blood with separation by iron hydroxide co-precipitation and analysis by multi-collector ICP-MS. This method was developed and has been used for several years for analyzing samples for Project 1.

Additional research focused on developing and evaluating methods for reliably preserving and analyzing inorganic and organic arsenic species in groundwater and sediment samples. We systematically assessed the performance of selectively packed cation and anion exchange columns (All Tech) for separation of arsenic species both in the laboratory and in the field. The effectiveness of using EDTA to prevent iron from precipitating (and bringing arsenic with it), and its effect on column separation efficiency have been evaluated. Preliminary results on Vineland, NJ, arsenic-contaminated groundwater suggest good recovery rates on spiked species and satisfying speciation separation. We also carefully evaluated the so-called "Ficklin" column (AG1x8, acetate form resin) for As(V) and As(III) separation for groundwater samples and phosphate extraction solution of sediments, and used the developed protocol to assess the arsenic species in natural and laboratory incubated Bangladesh sediments.

Core C: Hydrogeology Research Support Core Laboratory

M. Stute, P. Schlosser, M. Steckler

The Hydrogeology Support Core provides information on the groundwater and surface water flow and transport regime at our field sites in the US and Bangladesh, and supports projects number 5, 6, and 7.

Our continued focus this past year has been on hydraulic and tracer studies, as well as groundwater flow and transport modeling. We have continued to collect hydraulic head time series data from our well nests and a series of private wells in Bangladesh. We also collected monthly precipitation amounts and samples for stable isotope measurements at our monitoring station in Dhaka and conducted several sample collection campaigns.

A study by postdoctoral researcher Saugata Datta compared the stable isotope (^{18}O, ^{2}H) composition of precipitation and surface waters with that of groundwater in Araihazar and showed that whether the source of groundwater is directly recharged from precipitation or from surface waters, some of which may be ponds or fields created by irrigation, does not seem to be an important factor in Arsenic mobilization in this area.

This finding does not support the hypothesis that recharge from organic-rich surface water bodies created by irrigation is responsible for elevated dissolved As concentrations in our area.

Allan Horneman, a graduate student in the Department of Earth & Environmental Engineering defended his PhD thesis in December 2005. He explored tracer and modeling techniques in Bangladesh to better understand the dynamics of the groundwater flow system. In order to address the utility of SF_6 as an inexpensive age tracer in Bangladesh, he determined SF_6, noble gas, and ^3H concentrations of groundwater from two well nests in Bangladesh. He found that SF_6 ages were often too high relative to the $^3H/^3He$ ages. By using SF_6 solubility data generated by undergraduate student Jennifer Ivanowski, he excluded the possibility that peat was responsible for the retardation of SF_6. However, a simple model that incorporated a continuous gas exchange with pre-1965 trapped air with an air-to-water ratio of 0.02-0.1 is consistent with the observed SF_6 deficiencies. This study indicates that further studies are needed to better understand the behavior of SF_6 in Bangladesh ground waters before a widespread use can be recommended.

Allan also created a 3-D model for groundwater flow in the shallow aquifer for a 7 km^2 area in the Araihazar study area. The model incorporates properties of the surface cover, hydraulic conductivities, thickness of shallow aquifer, daily precipitation, evapotranspiration, and bi-weekly measurements of river levels. It uses observed well hydraulic heads and groundwater tracer ages as calibration targets. The results indicate a net recharge of the shallow aquifer of 27 cm yr^{-1}, which is strongly affected by irrigation. The horizontal distance a parcel of water has traveled from the surface to pumped shallow wells range from less than 40 m in the upper-most part to more than 350 m below a depth of 20 m. A comparison of modeled groundwater age with As distributions shows a correlation roughly consistent with the dissolved As versus $^3H/^3He$ age relationship found in drinking water and observation wells in Araihazar.

SBRP Training Core

The Training Core continued its Workshop Program with a week-long workshop from November 14-18 on “Hazardous Waste Operations First Responder Awareness and Hazard and Spill Control Training” given by Dr. Marco Pedone, an expert on hazardous waste management. In addition to covering the didactic requirements for NIOSH/OSHA/USCG/EPA training in this area, the workshop included a day-long simulation of a hazardous waste management exercise with assessment and clean-up as well as a medical emergency event. Besides the monthly Superfund Seminar Series, the Training Core also participated in the Annual Granville H. Sewell Distinguished Lecture In Environmental Health Sciences which this year featured Professor Peter Singer from Princeton speaking on “The Ethics of What We Eat” concerning the importance of food issues in environmental health. In addition, the Training Core continued to offer trainees participation in a web-based course on “Hazardous Waste

and Public Health" during the summer semester which can be done by anyone with a computer and internet access from any location and which has proven highly successful in past years. The course includes practical case studies in managing hazardous waste issues as problem-solving exercises for the participants. Finally, trainees participated in a day-long field trip to the United Nations for a tour and briefings on environmental health aspects of the Millenium Development Goals.